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Assessing the biological reactivity of organic compounds on volcanic ash: implications for human health hazard

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Abstract

Exposure to volcanic ash is a long-standing health concern for people living near active volcanoes and in distal urban areas. During transport and deposition, ash is subjected to various physicochemical processes that may change its surface composition and, consequently, bioreactivity. One such process is the interaction with anthropogenic pollutants; however, the potential for adsorbed, deleterious organic compounds to directly impact human health is unknown. We use an *in vitro* bioanalytical approach to screen for the presence of organic compounds of toxicological concern on ash surfaces and assess their biological potency. These compounds include polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (dlPCBs). Analysis of ash collected in or near urbanised areas at five active volcanoes across the world (Etna, Italy; Fuego, Guatemala; Kelud, Indonesia; Sakurajima, Japan; Tungurahua, Ecuador) using the bioassay inferred the presence of such compounds on all samples. A relatively low response to PCDD/Fs and the absence of a dlPCBs response in the bioassay suggest that the measured activity is dominated by PAHs and PAH-like compounds. This study is the first to demonstrate a biological potency of organic pollutants associated with volcanic ash particles. According to our estimations, they are present in quantities below recommended exposure limits and likely pose a low direct concern for human health.

Keywords Volcanic ash · Urban pollution · Health hazard · Organic compounds · Bioreactivity · CALUX bioassay

Introduction

Volcanic ash is a product of explosive volcanic eruptions and lava dome collapses and poses a threat to human health, infrastructure, air traffic and agriculture (Wilson et al. 2012,

2015). Ash can reach, and potentially affect, communities hundreds of kilometres from a volcano (Martin et al. 2009), and often remains in the environment for months or even years following deposition (Durant et al. 2012). Hence, people can be exposed to ash in the aftermath of an eruption but also later, due to resuspension by wind or human activity (Jarvis et al. 2020). The respiratory health effects following

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inhalation of volcanic ash are a long-standing and continuous global concern (Horwell and Baxter 2006; UNISDR 2015). Occurrence of respiratory symptoms varies among studies, but it is relatively clear that acute exposure to volcanic ash can exacerbate pre-existing respiratory diseases, such as asthma and bronchitis (Horwell and Baxter 2006).

With many volcanoes situated near large cities (Heiken 2013), ash frequently interacts with the atmosphere and associated anthropogenic pollution before being inhaled. Accordingly, populations are commonly exposed to volcanic ash concomitantly with additional substances, notably urban air pollutants such as vehicle and industry emissions, which are composed of a mixture of particulate matter and gaseous/volatile species. Currently, limited understanding exists regarding the human health hazards associated with the combined exposures to volcanic particulate matter and the polluted urban environment (Tomašek et al. 2016, 2018). Of particular importance is how volcanic ash interacts with urban pollutants and if this association may influence its biological reactivity and, in this way, contribute to an increase in adverse health effects for exposed populations.

Upon injection into the atmosphere, ash undergoes various physicochemical processes during transport and deposition that change its surface composition and reactivity (Ayrís and Delmelle 2012). Studies have recognised the role of volcanic ash in the scavenging of volatiles (such as sulphur and halogen gases and metals) from the atmosphere and in the dispersal of adsorbed materials into the environment (Witham et al. 2005; Ayrís and Delmelle 2012). Ash particles may also interact with anthropogenic pollution, which can be substantial in urbanised areas. We hypothesise that, during this process, organic compounds of toxicological concern to human health, such as dioxins (polychlorinated dibenzo-*p*-dioxins and dibenzofurans; PCDD/Fs), dioxin-like polychlorinated biphenyls (dlPCBs), polycyclic aromatic hydrocarbons (PAHs) and PAH-like compounds can be adsorbed onto ash surfaces.

Dioxins and dioxin-like compounds are ubiquitous environmental pollutants, characterised by high chemical stability, long-range transport and dispersal capability, low solubility in water and a tendency to accumulate in the environment (Jones and De Voogt 1999). Human exposure to PCDD/Fs and PCBs (via inhalation and ingestion of contaminated food) has been linked to a wide variety of health effects, including developmental and reproductive defects, alterations in immune function, cardiovascular disease and cancer (White and Birnbaum 2009; WHO 2019). These compounds are mainly formed as unintended by-products of anthropogenic activities such as industrial, municipal and domestic incineration and combustion processes (Safe 1998; Anderson and Fisher 2002), and PCBs have been produced commercially

in the past (Voogt and Brinkman 1989). Although banned worldwide, PCBs continue to be used in operating electrical equipment (e.g. transformers and capacitors) which have a limited service life (Harrad et al. 1994). There is evidence that dioxins are emitted from natural sources, such as wildfires (Crummett 1982; Meyer et al. 2004), to a much smaller extent, but no studies demonstrating their formation in volcanic eruptions have been published. Pyrolysis of vegetation, combustion processes and urban traffic are also responsible for the production of PAHs (Pereira et al. 1980; Howsam and Jones 1998), which are well known for their negative health implications, notably their genotoxic and carcinogenic potential (IARC 1983; Rengarajan et al. 2015).

It has been recognised that inhalation of particles with such adhered organic species can affect particle-cell interactions and can cause damage to lung cells and tissues (Fubini 1997; Knaapen et al. 2004). There is, thus, reasonable cause for concern if they are delivered to the body bound to the surface of volcanic ash particles following a volcanic eruption. Yet, compared to the other adsorbed hazards usually analysed on volcanic ash (e.g. potentially toxic elements such as As, Fe, Pb, F) (Stewart et al. 2020), the presence of persistent organic pollutants on ash surfaces and their potential impact on the health hazard have been poorly investigated, to date. Only a limited number of studies have identified PCDD/Fs, PCBs and PAHs adsorbed onto volcanic ash, which were shown to originate from anthropogenic sources (Lamparski et al. 1990; Takizawa et al. 1994; Stracquadanio et al. 2003; Guíñez et al. 2020), but none has considered their *in situ* reactivity and the consequential impact of exposure to such particles on human (and environmental) health.

The aim of this study was to screen volcanic ash for the presence of deleterious organic compounds typical of urban environments (such as PCDDs/Fs, PCBs and PAHs) and estimate their bioreactivity using an *in vitro* bioanalytical approach. We utilised a reporter-gene cell-based bioassay, the Chemically Activated Luciferase gene eXpression (CALUX) (Denison et al. 2004), which is based on the interaction of compounds with the aryl hydrocarbon receptor (AhR), a protein that is responsible for mediating the toxic and biological effects of diverse organic compounds (Denison et al. 2011). We assayed a selection of volcanic ash samples collected near urbanised areas from active volcanoes (Etna, Italy; Fuego, Guatemala, Kelud, Indonesia; Sakurajima, Japan and Tungurahua, Ecuador) to determine whether the occurrence of organic compounds on ash is common. The experiments provide the first direct evidence of the biological potency of ash-associated organic compounds and provide an avenue in which to investigate the potential health implications of their association.

Materials and methods

Volcanic ash samples

We selected five active volcanoes for this study, ranging in magma composition and eruption styles: Etna — ET, Fuego — FU, Kelud — KE, Sakurajima — SA and Tungurahua — TU (Table 1). The ash samples are from variable proximities to urban areas and include samples ranging from pristine (freshly erupted samples that have not been rained on) to older deposits (exposed to meteorological conditions for a few weeks or months; Table 1). Samples were not collected specifically for this study but were provided in varying amounts and analysed in their bulk (un-sieved) form, except for samples TU1 and SA1, which were provided in dry-sieved fractions < 63 µm and < 125 µm, respectively. We acknowledge this as a limitation of the study as, ideally, the analysed samples would be of a consistent size fraction and one that directly reflects the respiratory hazard, such as the ‘respirable’ fraction, which is defined as particles that can penetrate to, and deposit in, the deep lung (sub-4-µm aerodynamic diameter) (ISO 1995). However, isolation of respirable material from bulk ash (as in Tomašek et al. 2016) in amounts sufficient for this analysis was not possible due to the varying quantities of sub-4-µm material among the samples and limited amounts of volcanic ash available for the study. It is important to note that organic compounds have been found to be enriched in the finer fractions of other

particulate matter (Nessel et al. 1992; Kaupp and McLachlan 2000), so our measured values (section ‘CALUX analysis of volcanic ash’) may be a low estimate.

Particle size distributions and specific surface areas were assessed on sub-samples for all ash samples in the study. Particle size distributions were determined using a Coulter LS230 (Beckman Coulter Inc., USA) in water without sonication, at the Vrije Universiteit Brussel, Belgium. Data were analysed according to the Mie theory of light scattering, with a refractive index set to 1.63 and an absorption coefficient of 0.1 (Horwell 2007). Results are the mean of three consecutive runs of the sample. Specific surface area (SSA) was determined according to the BET method (Brunauer et al. 1938) and analysed by nitrogen adsorption using a custom-made laboratory gas sorption analysis system at the University of Lille, France (Joshi et al. 2017). Results are the mean of three independent measurements of the sample.

CALUX bioassay

The CALUX bioassay uses a mammalian cell line that is genetically modified to produce a quantifiable response following activation of the AhR signalling pathway. Activation of AhR by a compound results in induction of a reporter gene (luciferase) within the cells and the activity of the resulting enzyme (luciferase) produces light which is quantified using a luminometer. The amount of induced luciferase is directly proportional to the amount and potency of the AhR-active

Table 1 Sample and collection information for the volcanic ash samples analysed in this study. Samples range from pristine (freshly erupted samples that have not been rained on) to older deposits

Sample name	Volcano	Eruption date	Collection date	Type of activity	Magma type	Collection location	Distance from vent (km)	Collection environment	State of sample
ET1	Etna	03-Nov-02	03-Nov-02	Strombolian	Trachybasalt	Catania, Italy	25.4	Urban	Pristine
ET2		11-Dec-02	11-Dec-02	Strombolian	Trachybasalt	Catania, Italy	26.7	Urban	Pristine
FU1	Fuego	03-Jun-18	24-Oct-18	Paroxysmal	Basalt	Alotenango, Guatemala	7.3	Urban	Not fresh
KE1	Kelud	13–15-Feb-14	15-Feb-14	Plinian	Andesite	Yogyakarta, Indonesia	210	Urban	Pristine
KE2		13–15-Feb-14	01-Apr-14	Plinian	Basaltic andesite	Yogyakarta, Indonesia	210	Urban	Rained on
SA1	Sakurajima	18-Jul-13	18-Jul-13	Vulcanian; co-PDC ash	Andesite	Kurokami Observatory, Japan	4	Suburban	Pristine
SA2		31-Oct-10	31-Oct-10	Vulcanian	Andesite	Arimura Observatory, Japan	2.3	Suburban	Pristine
TU1*	Tungurahua	02-Feb-14	07-Feb-14	sub-Plinian; co-PDC ash	Andesite	Los Pacharos, Ecuador	6	Rural	Pristine

*The sample TU1 is also called 14TUN05 in other publications using the same sample (Müller et al. 2020; Yang et al. 2020)

compounds to which the cells have been exposed (Denison et al. 2004; Windal et al. 2005).

This bioassay is widely applied for screening and monitoring of diverse biological and environmental materials, including atmospheric particulates (Denison et al. 2004; Gizzi et al. 2005; Khedidji et al. 2017), and offers a novel strategy for volcanic material characterisation. In comparison to conventional chromatography techniques, CALUX is a rapid and relatively cost-effective semi-quantitative screening method, which provides an integrated effect-based biological response of all compounds present in the sample extract that can bind to and activate the AhR. Thus, CALUX enables fast identification of samples containing chemicals of potential concern, and it is useful for making timely and informed decisions on the need for further analyses by chromatography techniques.

In this study, the CALUX bioassay was conducted using both crude (total) volcanic ash extracts (samples containing all extracted compounds) to determine the total AhR activity for a sample, and cleaned-up ash extracts (samples with PCDD/Fs and dI PCBs isolated from the total extracts) to determine the contribution of PCDD/Fs and dI PCBs to the total AhR activity. The analyses of crude extracts for total AhR activity were conducted on three replicate ash samples (i.e. three separate ash extractions). The analyses of cleaned-up extracts for PCDD/Fs and dI PCBs were done on three replicate samples for FU1 and KE2 but only on a single replicate sample for all other samples due to the limited amounts of volcanic ash available for the study.

Each sample extract was then tested in 10 concentrations (in triplicate) to establish a concentration–response curve (see ‘Results’ section, Figs. 2 and 3) by plotting the measured luciferase activity (luminescence) expressed as a fold change from the assay background value. The response induced by each sample was then compared to the response of reference compounds, which were used to derive standard curves. These reference compounds were benzo[a]pyrene (BaP) for total AhR activity (crude extracts), and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD; the most potent dioxin congener) for PCDD/Fs and dI PCBs (cleaned-up extracts). Through this comparison, the AhR activity of a sample was converted into bioanalytical equivalent (BEQ) concentration and expressed as ng BaP or pg TCDD equivalent per g of ash dry weight (see ‘Results’ section, Table 4). We refer the reader to Appendix 1 for a detailed methodology on ash extraction, clean-up, AhR-CALUX procedures and data analysis.

Results

Volcanic ash properties

Particle size analysis showed that all the samples except ET2 contain inhalable (sub-100 µm) particles, at varying

volume percentages (Fig. 1, Table 2). The SSA of samples varied among the samples and ranged from 0.07 to 1.84 m²/g (Table 3).

CALUX analysis of volcanic ash

Illustrative concentration–response curves (relative response as a function of the concentration) for crude and cleaned-up extracts of samples, and their corresponding standard curves, are shown in Figs. 2 and 3, respectively. All crude extracts induced a response in the bioassay, indicating the presence of AhR-active compounds on each of the ash samples (Fig. 2). Relative response levels calculated for these sample extracts ranged between 6 and 21 ng BaP BEQ/g, with the exception of sample KE2, which was the most potent, with a BEQ of 122 ng BaP BEQ/g (Table 4). Low levels of AhR activation were detected in the PCDD/Fs fraction of the cleaned-up sample extracts (Fig. 3), with response levels ranging between 0.2 and 0.6 pg TCDD BEQ/g (Table 4). The highest activities were measured in samples FU1 and KE2, with a BEQ of 0.3 and 0.6 pg TCDD BEQ/g, respectively (Fig. 3, Table 4). The dI PCBs fraction of the cleaned-up samples showed no detectable activity in the bioassay (*data not shown*), indicating the absence of dI PCBs or their presence below detectable levels in analysed samples.

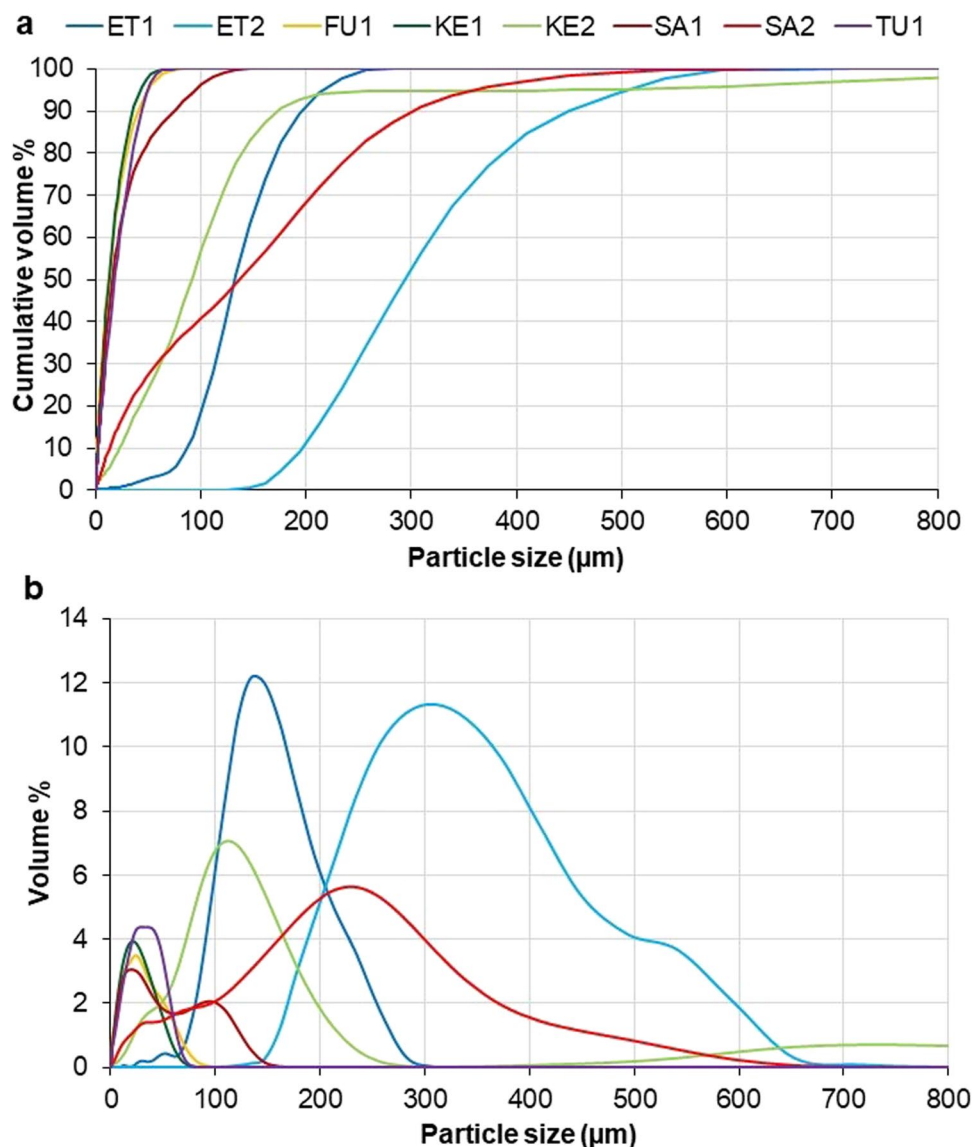
Discussion

Bioreactivity of organic compounds on volcanic ash

AhR is known to be activated by a wide range of structurally diverse chemicals (DeGroot et al. 2011), notably a very large and diverse collection of PAHs and chlorinated aromatics (Machala et al. 2001; Ziccardi et al. 2002; Ohura et al. 2007). The low level of AhR activity in the cleaned-up PCDD/Fs fraction (<0.6 pg TCDD BEQ/g) and lack of activity in the dI PCBs fraction indicates that the chemicals in these fractions (e.g. chlorinated, brominated and mixed chloro/bromo dibenzo-*p*-dioxins, dibenzofurans, biphenyls and related halogenated aromatic hydrocarbons) contribute little to the overall AhR activity of the total extract, where response levels were up to 122 ng BaP BEQ/g. This suggests that the vast majority of the total measured AhR activity can be attributed to PAHs and PAH-like compounds. This observation is supported by past identification of PAHs on volcanic ash (Pereira et al. 1980; Stracquadanio et al. 2003; Guíñez et al. 2020) and the fact that they are typically far more abundant in the environment (Lohmann et al. 2000).

Direct comparison of our data with those of previous studies that measured organic compounds on volcanic ash is hindered by the use of different methods and associated differences in concentration reporting. Previous studies

Fig. 1 Particle size distributions of ash samples from Etna (ET), Fuego (FU), Kelud (KE), Sakurajima (SA) and Tungurahua (TU) volcanoes. (a) Cumulative particle size distributions and (b) particle size distributions of samples. Lines represent the mean of three measurement cycles recorded for each sample



utilised instrumental analysis techniques, namely gas chromatography/high-resolution mass spectrometry (Pereira et al. 1980; Takizawa et al. 1994; Kozak et al. 2017) and

Table 2 Particle size information at health-relevant size fractions for the analysed samples. Data are the mean of $n=3$

Sample	Particle size (μm; cumulative vol. %)				
	< 1	< 2.5	< 4	< 10	< 100
ET1	0.04	0.11	0.18	0.28	18.38
ET2	0.00	0.00	0.00	0.00	0.00
FU1	6.74	16.76	23.06	43.16	100.00
KE1	4.93	12.65	19.19	41.43	99.98
KE2	1.05	1.97	2.50	4.33	56.62
SA1	3.49	10.59	16.37	35.75	96.18
SA2	0.97	2.12	3.16	7.68	40.80
TU1	2.90	9.38	14.19	30.45	99.99

high-performance liquid chromatography (Stracquadanio et al. 2003; Guíñez et al. 2020), which allow the identification and quantification of individual chemicals in sample extracts, but provide no direct information on sample bioreactivity. Only Takizawa et al. (1994) reported their

Table 3 Specific surface area (SSA) of ash samples used in the study. Data are the mean of $n=3 \pm$ standard deviation

Sample	SSA (m ² /g)
ET1	0.07 ± 0.04
ET2	0.11 ± 0.03
FU1	1.36 ± 0.05
KE1	0.82 ± 0.06
KE2	0.54 ± 0.10
SA1	0.81 ± 0.11
SA2	1.84 ± 0.07
TU1	0.73 ± 0.19

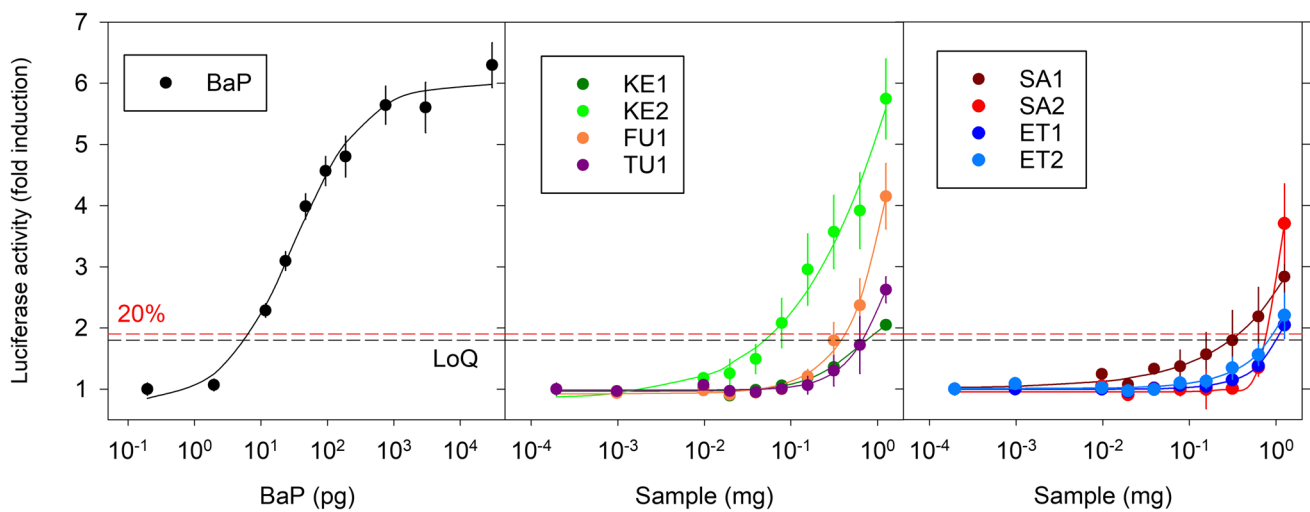


Fig. 2 Luciferase induction in cells by BaP (reference compound) and volcanic ash crude (total) extracts as determined by CALUX. The figure shows illustrative concentration–response curves for BaP standard and volcanic ash crude extracts (total AhR activity). Luciferase activity of BaP and samples was expressed as a fold change from the

background value. The red dashed line represents the induction (20%, at 1.9-fold change) used to derive the BEQ value for the samples. Limit of quantification (LoQ) was equal to 1.8-fold change (the black dashed line)

findings on Sakurajima ash as TCDD toxicity equivalents (TEQs), which generally correlate well with CALUX BEQs (US EPA 2014a). They found PCDD/Fs concentrations of approximately 0.03 pg TCDD TEQ/g (5 pg/g ash), which are much lower than those in the Sakurajima ash analysed here (0.23 pg TCDD BEQ/g; Table 4). Our finding of AhR activity in Etna samples is in agreement with past reports from Stracquadanio et al. (2003) who also analysed ash from Etna, including a sample collected in Catania, Italy. From their samples, they reported concentrations of eight PAHs

(from the US EPA Priority Pollutant List; US EPA 1982) ranging from 0.2 to 20 ng/g ash, the majority of which are known to activate the AhR signalling pathway.

No correlation was observed between our BEQ values and the physical properties measured (sample SSA, Fig. A2.1, and particle size distributions, Fig. A2.2; see Appendix 2). Ash chemical properties, such as surface composition and reactivity, are central to the uptake of atmospheric/ambient species (Maters et al. 2016; Urupina et al. 2019) and may also play a role in adsorption of the organic compounds

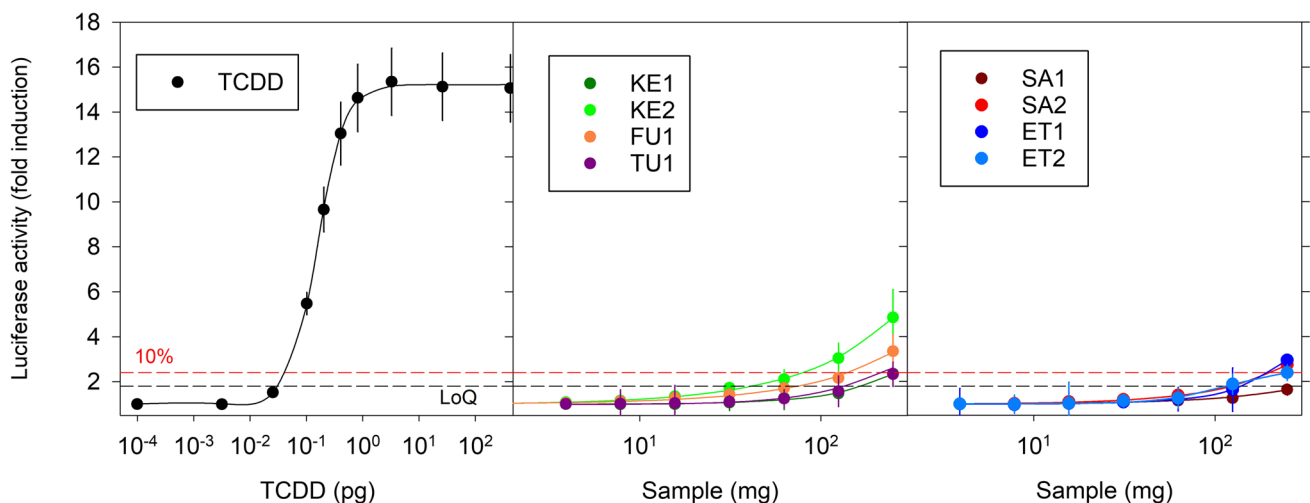


Fig. 3 Luciferase induction in cells by TCDD (reference compound) and PCDD/Fs from volcanic ash extracts as determined by CALUX. Illustrative concentration–response curves for TCDD standard and PCDD/Fs fractions of sample extracts. Luciferase activity of sam-

ples was expressed as a fold change from the background value. The red dashed line represents the induction (10%, at 2.4-fold change) used to derive the BEQ value for the samples. Limit of quantification (LoQ) was equal to 1.8-fold change (the black dashed line)

tested here. Such an exhaustive ash surface characterisation may provide further information regarding sequestration or exposure but was beyond the scope of this bioanalytical screening study. Therefore, we cannot comment further on the influence of ash properties on the adsorption of organic compounds. However, considering the finding of AhR-active compounds in both pristine and non-pristine ash samples (Table 4), and the lack of correlation found with physical properties, we assume that the observed variability in the amounts of adsorbed pollutants is due, at least in part, to varying atmospheric composition (i.e. pollutant concentrations), on the spatial- and temporal-scale. Concentrations of PCDD/Fs and PAHs in the ambient air highly depend on the (local) emission rates and environmental conditions (Lohmann and Jones 1998; Ravindra et al. 2008) which, in turn, would impact adsorbed abundances. KE2 had by far the highest measured AhR activity in crude extract (122 ng BaP BEQ/g), and this sample was collected several weeks following the eruption (Table 1). Another non-pristine sample analysed in this study, FU1, exhibited relatively high total AhR activity (16 ng BaP BEQ/g). This suggests that a longer residence time in the environment (i.e. in ashfall deposited prior to collection) may lead to greater adsorption of organic pollutants onto ash surfaces. However, it remains to be investigated if the adsorption indeed occurs mostly after deposition or during airborne transport. The specific influence of sample history offers another promising avenue to explore and is particularly relevant for long-term exposure to resuspended ash (Jarvis et al. 2020).

Implications for human health

Most of the analysed samples contain inhalable (sub-100 μm) particles, ranging from 18 to 100% by volume (Fig. 2), which indicates their potential to be inhaled. The percentage of respirable (sub-4 μm) particles varied among

samples (0.1–23% by volume; Table 2). This variability in fine particle content reflects multiple factors, including, but not limited to, the sample collection distance from the vent and the magnitude and explosivity of the eruption (Horwell and Baxter, 2006; Horwell 2007). The mass of respirable ash that deposits in the lungs from exposure is difficult to estimate, owing to a lack of empirical data on real-life exposure levels. Airborne ash concentrations are rarely measured and personal exposure to volcanic ash is highly influenced by the activities undertaken by individuals, including the use of exposure reduction measures (e.g. staying indoors, wearing facemasks) (Searl et al. 2002; Horwell et al. 2003; Steinle et al. 2018). Furthermore, the depositional efficiency of ash in the lung as a poly-disperse granular material is largely unconstrained (Lahde et al. 2013). However, it is informative to contextualise the BEQ values determined in this study, and some assumptions can be made to allow an evaluation of the potential health hazard.

For this purpose, we calculated a daily intake of PCDD/Fs and PAHs via inhalation of volcanic ash. We based the calculation on a daily inhaled air volume of 20 m^3 , defined for an adult (US EPA 2014b), an assumed 2-h daily exposure to airborne ash concentrations of 0.02 and 1 mg/m^3 , which correspond to a case example of minimum and maximum daily averages (Searl et al. 2002), and a lung deposition efficiency for ash of 10% (Lahde et al. 2013). Use of the maximum BEQ for PCDD/Fs measured in this study (0.6 pg TCDD BEQ/g) equates to inhalation of 1×10^{-4} pg TCDD BEQ/day when ambient concentrations of ash are high (1 mg/m^3) and 2×10^{-6} pg TCDD BEQ/day when ambient concentrations are low (0.02 mg/m^3). The maximum BEQ for PAHs measured in the study (122 ng BaP BEQ/g) equates to a daily intake of 20.4 pg BaP BEQ and 0.4 pg BaP BEQ for high and low concentrations of airborne ash, respectively.

Table 4 CALUX analysis results expressed as bioanalytical equivalent concentration (BEQ \pm the standard error (SE) and relative standard error (RSE)) on a per mass and surface area basis relative to BaP for total AhR activity (ng/g and ng/ m^2) and relative to TCDD for PCDD/Fs (pg/g and pg/ m^2)

Sample	Crude extract (total AhR activity)			Cleaned-up extract (PCDD/Fs*)		
	ng BEQ BaP/g (\pm SE ^a)	RSE %	BEQ ng/ m^2	pg BEQ TCDD/g (\pm SE ^b)	RSE %	BEQ pg/ m^2
ET1	6 \pm 0.7	12	85.7	0.23 \pm 0.01	6	3.29
ET2	7.3 \pm 1.1	15	66.4	0.19 \pm 0.04	21	1.73
FU1	16.4 \pm 2.2	13	12.1	0.33 \pm 0.04 ^a	12	0.24
KE1	7.9 \pm 2.1	27	9.6	0.18 \pm 0.01	7	0.22
KE2	122 \pm 29	24	225.9	0.6 \pm 0.07 ^a	12	1.11
SA1	21 \pm 6	29	25.9	< LoQ	-	-
SA2	8.2 \pm 0.4	5	4.5	0.23 \pm 0.02	9	0.13
TU1	9.2 \pm 1.2	13	12.6	0.18 \pm 0.02	8	0.25

SE was derived from either three independent ash extractions^a or from three replicate measurements of a single extraction^b. *The response for dIPCB fractions was below quantification limit (LoQ; Appendix 1) and therefore not expressed as BEQ

Quantitative data on pulmonary bioavailability of PCDD/Fs and PAHs following inhalation exposure in humans are limited, so we based the risk calculations on the assumption that 100% of the particle-bound dose is absorbed (Nessel et al. 1992). With insufficient toxicokinetic information for inhalation exposure, route-to-route extrapolation was made to ingestion, which is the main exposure route for organic contaminants. This was considered appropriate given that the critical effect is not specific to the site of application. Tolerable daily intakes (TDI) for ingestion of organic contaminants are normally expressed on a body-weight (bw) basis and are defined as the amount of a substance that can be ingested in a period of 24 h without appreciable health risk (WHO 1994). Calculated on the basis of default values for population body weight reported by the European Food Safety Authority (EFSA 2012), daily intakes for an adult (70 kg) of PCDD/Fs for the high concentration of airborne ash equate to 1.4×10^{-6} pg TCDD BEQ/kg bw/day, whereas the intake of PAHs is 0.3 pg BaP BEQ/kg bw/day. Referencing the WHO guideline values of 10–40 pg of TCDD/kg bw/day (van Leeuwen et al. 2000) and 100 µg of BaP/kg bw/day (JECFA 2006), the measured values are far below the TDI. Considering that the exposure to airborne ash is typically of limited duration, whereas the guidance values for health-based exposure limits relate to long-term exposure, it can be said that direct exposure to PCDD/Fs and PAHs via inhalation of ash likely represents a low immediate concern for human health.

Future work perspectives

Our study confirmed that ash can scavenge organic pollutants from the atmosphere which, upon ash deposition, may promote contact with soil, vegetation and water where they then can be taken up in the food chain (Dumortier et al. 2012). Ingestion of contaminated food represents the major route of human exposure to dioxins and dioxin-like compounds (Van den Berg et al. 2006). Adsorption onto ash is also a method by which these compounds can be spread over large geographical areas, especially if ash remains in the environment over a longer period of time. Once associated with particles, these compounds degrade slowly and may persist for many years, which has been demonstrated by measurements of PAHs, PCDD/Fs and dioxin-like compounds in soil, sediments and urban air particles (e.g. soot particles, road dust) (WHO 2000, 2019). The potential for volcanic ash to contribute to sediment concentrations of dioxin and dioxin-like compounds at our sampling locations would require a different analytical and sampling approach, but may be of potential future interest given these screening data.

The findings of our study open the opportunity for more detailed research. From the present results, it is not possible to directly elucidate the origin (volcanic or anthropogenic)

of organic pollutants on ash nor can it be excluded that, in addition to volcanic particles, our samples may have contained some urban aerosol particles. A follow-up study should, therefore, implement an appropriate sampling strategy including environmental background sampling and, possibly, direct sample collection from the air. Moreover, a future study should investigate samples from a recent eruption, collected at different distance from the source volcano and at regular time intervals to elucidate the critical factors controlling the presence and abundance of organic compounds (e.g. grain size, ash composition, meteorological conditions, exposure to anthropogenic contamination).

Conclusion

This study provides the first evidence of the biological potency of organic pollutants associated with volcanic ash particles. We find bioactive PAHs and, to a lesser degree, PCDD/Fs associated with ash samples from five separate locations. According to our calculations, they are present in quantities below recommended exposure limits and, therefore, likely pose a low direct concern for human health. However, previous work has shown a synergistic toxic effect between volcanic ash and other organic constituents (Tomašek et al. 2016), and so these data should be considered in context. The findings of this first study provide a novel basis on which to understand the ways in which ash interacts with organic pollutants and how they may contribute to ash toxicity. This is crucial for a mechanistic understanding of ash toxicity, which is currently lacking.

Very little is known about the concentrations and origins of PAHs, dioxin-like compounds (PCDD/Fs and PCBs) and related chemicals on volcanic ash and their implications for human health. We were unable to correlate the specific influence of sample histories (eruption type, collection place and time) or physical properties of our ash samples (particle size distribution, specific surface area) with the measured abundance of organic compounds. However, our successful application of the AhR-CALUX bioassay to volcanic ash establishes a fast, cost-effective method which, accompanied by systematic sampling, can be used in future studies to monitor the pollutant transport and deposition in the environment following an eruption. This represents an important step in the ongoing efforts to identify and characterise volcanic ash properties that may be of relevance for adverse health effects, and for the implementation of screening strategies for protecting communities affected by ashfall.

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Data availability The datasets generated during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests The authors declare no competing interests.

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